

## PRODUCTION OF ENVIRONMENTALLY INNOCUOUS COATINGS

Emilio Eguía López<sup>1</sup> y Alfredo Trueba Ruiz<sup>2</sup>

### ABSTRACT

It is known the biofouling phenomenon, as well as the negative consequences that it means for the artificial structures in contact with seawater in form of structural defects and of additional expenses for the companies which develop their work in the marine scope due to the processes of cleaning and prevention, the evolution in the world of the technology of antifouling paintings, once we analysed the serious environmental problems caused by an indiscriminate use of biocides of high toxicity in its composition as they are the organic derivatives of tin compounds made up and of the uncontrolled emission of volatile organic compounds (VOC) to the atmosphere, according to the present environmental norm, has as only aim to develop environmentally innocuous coverings based on water in which extracts of the very same marine world are used as biocides compounds.

**Key words:** Biofouling, antifouling coatings, organic by-products of tin compounds, volatile organic compounds (VOC), environmental norm

### 1. INTRODUCTION

Any artificial structure in contact with seawater is rapidly coated by a microbiological biofilm, which serves as a base for macro-organisms to grow on. This phenomenon, known as biofouling, causes structural problems and its mitigation involves a severe economic outlay for the industries, which operate in the marine environment.

Biofouling can be defined as «*the undesirable phenomenon of adherence and accumulation of biotic deposits on a submerged artificial surface or in contact with seawater*». This accumulation or incrustation consists of a film composed by microorganisms affixed to a polymeric matrix created by themselves (biofilm), where inorganic particles (salts and/or corrosion products) may arrive and be retained, as a consequence or other types of fouling developed in the course of the process. This biofilm composed of microorganisms (microbial biofouling or *microfouling*) can originate the accumulation of macro-organisms (macrobial biofouling or *macrofouling*) (Eguía, 1996).

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<sup>1</sup> Catedrático de Universidad. Department of Sciences and Techniques of Navigation and Shipbuilding. University of Cantabria. Tel. 942201328, Fax. 942201303, C/Gamazo, N°1, 39004 Santander, Spain. [emilio.eguia@unican.es](mailto:emilio.eguia@unican.es)

<sup>2</sup> Doctor en Ciencias del Mar. Profesor Asociado. Department of Sciences and Techniques of Navigation and Shipbuilding. University of Cantabria. Tel. 942201332, Fax. 942201303, C/Gamazo, N°1, 39004 Santander, Spain. [alfredo.trueba@unican.es](mailto:alfredo.trueba@unican.es)



Biofouling is made up of hundred of species such as tubícolas bacteria, protozoas, seaweed, molluscs, briozoas, cirripeds, polychaetes, ascidias, hidrozoas, etc. These organisms adhere themselves to the substrate developing a fast growth and great reproductive potential, being demonstrated the strategy of the different families in order to obtain the resources that the ecosystem offers, avoiding the competition among them by means of the differentiation of the periods of colonisation, in such a way, that the incrustation begins with the settling of the fitobentónicos organisms during the springtime, to continue with the adhesion of the zoobentónicos organisms next (García P, 1996).

Therefore, biofouling accelerates the processes of corrosion of the materials and causes losses in the operative effectiveness of the structures. These damages take place on movable and stationary structures affecting boats, petroliferous or gas platforms, oceanographic investigation implements, thermal energy conversion plants and subaqueous sounding equipment. It also damages maritime cultivation facilities (aquariums, cages, conduits, and pumps) as well as the same cultivated organisms.

In ships the friction between the hull and the water increase, which means an increase in fuel consumption (up to a 40–50% with little dense biofouling) and there is a decrease in speed and manoeuvrability. The hull of a ship unprotected by antifoulings systems, can accumulate up to 150 kg of biological incrustation by square meter during six months in the sea, which in a long tanker with 40,000 m<sup>2</sup> of underwater hull supposes an increase in weight of 6.000 metric tons of biological incrustations (OMI, 1999), which means enormous economic losses.

In order to avoid economic losses, as well as an accelerated deterioration of the artificial structures in contact with seawater, different types of protections have been used for long. Among them we must point out the copper coatings that began to be used by the Phoenicians and which continued being successfully used on wood ships until the 18<sup>th</sup> century. When iron ships were first built, paintings widely known as “patents” in which the copper sulphate acted as byocide principle began to be manufactured. From 1960 the use of paintings in whose composition we could find copper, mercury, arsenic, organic derivatives of tin (organic compounds of tin like tributyltin (TBT) and the trifeniltina (TPT)) spread widely, eventually, it has been proven that they were a real risk for the marine ecosystem.

In the seventies the use of antifoulings paints based on the byocide performance of the organic derivatives of tin extended, specially tributyltin (TBT), that is why most of the navigation ships covered their hulls with this type of paintings, which turned out to be effective and economic.

During the eighties we became aware of the consequences that the use of the TBT in antifoulings paintings was having on the marine ecosystems, specially in areas of low water interchange by tidal influence, such as bays or estuaries, where it is specially detrimental on the populations of some invertebrates, molluscs, crustaceans and fish, where very important malformations in some species were detected. As a result of the worries these facts arose, several countries introduced controls to limit the use of TBT in antifoulings



paints in small ships. Thus, in 1982, France prohibited the use of TBT in ships with an inferior length to 25 m, Japan, United Kingdom, the United States, Norway, Australia, New Zealand and other countries followed.

At the beginning of the nineties, an OMI resolution recommended governments to ban the use of tributyltin in ships within inferior length to 25 m and restrictions in the leaching process prevail of tributyltin are imposed, having to be inferior to 4 micrograms/cm<sup>2</sup> /day. In countries such as Japan, New Zealand and Australia the use of antifoulings that contain TBT (OMI, 1999) is forbidden.

Since 1997, Japan forbade to manufacture antifoulings paints that contain TBT, being January 1, 2003 the propose date for the prohibition of the organic derivatives of tin compound use like byocides in the antifoulings systems, being left for the year 2008 its total prohibition.

## 2. TECHNOLOGY OF ANTIFOULING PAINTS

The antifoulings paints are specially formulated to be applied on structures in contact with seawater in order to prevent the settlement of the marine organisms that compose biofouling (Arias, 1994).

They are widely known by the name of “patents” and as all the other paints come from a fixed vehicle, a volatile vehicle, pigments and additives. Once applied they make a film dry, uniform and well adhered to the substratum in order to protect it and when in contact with the seawater, they begin to release biologically active products that surround the surface treated within byocide dock that prevents the settlement of the organisms. The capacity of control of the level of liberation of the byocides substances will allow us to differentiate several types of antifouling paints, being the toxin concentration in the laminate waterproof cloak (painting surface in contact with the seawater) the one which determines the antifouling power of the painting. Factors like the speed of the ship, the temperature, salinity and pH of the seawater, light, levels of pollution, etc., are going to remarkably influence on whether the above toxin concentration is higher or lower.

We can classify the antifouling paints as “*no-smoothing*” of soluble or insoluble matrix and “*self-smoothing*”.

### 2.1. NO-SMOOTHING ANTIFOULING PAINTS WITH A SOLUBLE MATRIX

The toxin used is cupreous oxide and is dispersed in a water soluble vehicle, normally *colophony*. The colophony, being a smooth acid, will dissolve slowly when reacting with the seawater, which is a little alkaline. The dissolution of the vehicle will, as a consequence bring about, the dissolution of cupreous oxide, giving rise to the layer of “*laminate impact*”, the toxins becoming on micro-organisms contact. The reactions will, as a consequence bring about, the cupreous carbonate formation, which has the necessary toxic properties. In addition to the cupreous oxide, it is also necessary to use organic derivatives of tin compounds, at present no longer used on accost of their negative effects on the environment. These antifouling systems last between 9 and 12 months.

From a practical point of view, the advantages and limitations of this paints can be summarised as follows: (Guijarrubia, 1989)

- They can be applied on “soft” primers, on wooden or steel hulls
- They cannot be exposed to atmospheric oxygen for long periods of time, which is why the treated surface must be submerged only a few hours after the paint being applied
- The dissolution of the fixed vehicle progresses in an uncontrolled manner, which limits the predictability of the useful life of the film as an antifouling agent, depending on such factors as the speed of the ship, salinity, pH or on the action of bacteria on the vehicle
- The mechanical properties of the dry film and especially of the set of layers formed on the surface after successive paint applications can increase the average roughness of the hull in the case of a ship, when chipping and flaking, etc, occur. This makes it necessary to take off the old layer before applying the new one, with two new coats of paint being applied at a 48 hours interval, to a thickness of 40 microns of dry film per coat layer.

In figure I the state of the recently applied dry film is contrasted with the film after a period of time has passed, in which the fixed vehicle has been diluted and therefore part of bioactive compounds present in the film have been freed.

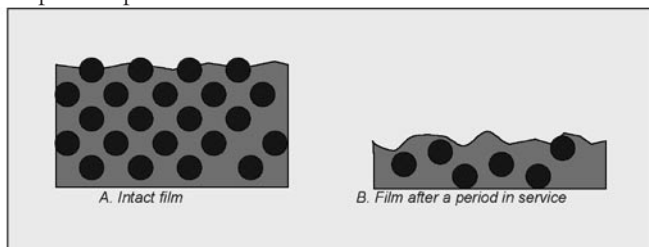


Figure 1. Mechanism of operation (soluble matrix)

## 2.2. NO-SMOOTHING ANTIFOULING PAINTS WITH AN INSOLUBLE MATRIX

They are constituted mainly by insoluble water resins, which dry physically (chlorinated rubber, acrylics, vinyls, etc.) mixed with small amounts of soluble resins (colophony and by-products) which, like the biocide compounds, are dispersed in the insoluble matrix. These paints absorb water and the soluble part of the resin gradually disintegrates, leaving an insoluble structure similar to a rigid sponge, full of water, through which the biocide products are dissolved, by diffusion (Arias, 1994).

The antifouling function is obtained by means of the diffusion of biocide compounds towards the external surface of the film in a process known as leaching. Figure II shows the evolution of the speed of leaching during the time the paint is in service: (Quirós, 1995)

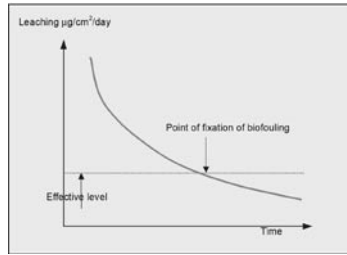


Figure 2. Typical leaching curve (insoluble matrix)

The advantages and limitations of this type of paints can be summarised in the following way:

- The leaching process is controlled.
- Due to their hard resin content, they can remain outdoors for up to two months without loss of their properties. They must be applied in two layers, to a thickness of 80 microns of dry film per layer and it will last from 12 to 24 months depending on the type of waters
- Once the paint has worn away, there is remains an insoluble resin porous structure that should be sealed with a suitable sealing paint before applying the new antifouling layers, since otherwise they would partially absorbed by the old paint.
- The content of biocide elements in the dry film is higher than in the case of those with a soluble matrix
- Their mechanical properties are high quality fixed vehicles bindings are used
- They cannot be applied on “soft” primers, since they contain strong dissolvents.

In figure III the state of the recently applied dry film applied is contrasted with the film after a period of time has passed, in which we can observe the effect of the leaching process of the paint.

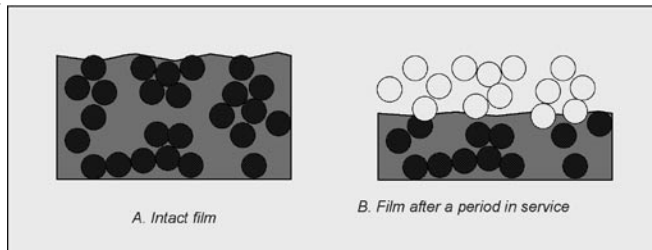


Figure 3. Mechanism of operation (insoluble matrix)

### 2.3. SELF-SMOOTHING ANTIFOULING PAINTS

These are products based on biocide polymers whose speed of dissolution can be controlled by affecting the physical-chemical process regulating. In this type of paint the toxic substance incorporated in the resin dissolves gradually, in a self-programmed way, by means of a hydrolysis reaction of the polymer when it comes into contact with seawater.

In addition to this, the biocide pigments that contained there also dissolve in a controlled fashion.

Figure IV shows the rate of toxic liberation during the time is in service the paint. (Quirós, 1995)

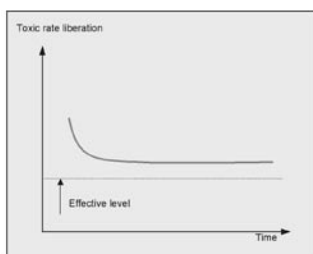


Figure IV. Typical leaching curve (self-smoothing)

The following characteristics of these paints should be emphasized:

- Although not a hard product, it permanently retains a certain plasticity that is accentuated when submerged in water, and can remain outdoors for up to 3 months without losing any of its properties
- They are applied in several layers to a thickness of a 100-150 microns per layer. It has durability directly proportional to its thickness: 100 microns/year (maximum of 5 years). Its surface once submerged and in good condition, is extraordinarily smooth, with excellent hydrodynamics properties, which helps towards the attainment of high speeds
- The average speed of biocide element liberation remains constant over time, which makes its antifouling function highly reliable
- In the case of a ship, layers through successive entrances to dock are not accumulated, which eliminates that factor of increasing roughness average of the hull
- When one layer of paint is put on top of another, all that is required is a pressure jet water wash down, without an intermediate sealing coat being necessary
- Self-smoothing antifouling paints, besides providing the hull with antifouling protection, offer the added benefit smoothing of their own external surface.

In figure V the state of recently applied the dry film is compared against the film after a period of time has passed, in which we can observe the effect of the leaching process of the paint.

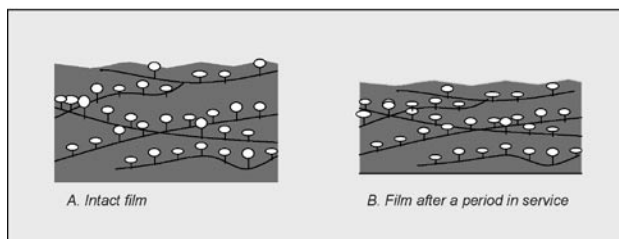


Figure V. Mechanism of operation (Self-smoothing)



### 3. CONSEQUENCES OF THE USE OF ORGANIC DERIVATIVES OF TIN COMPOUNDS SUCH AS BYOCIDES IN ANTIFOULING PAINTS

Generally speaking, all the organic compounds of tin, and especially tributyltin (TBT), are extremely toxic compounds, even at concentrations of only a few nanograms per litre. The organisms of the marine environment (from bacteria to fish) are affected by a wide range of harmful effects from sub-lethal to lethal. Their presence can be seen in alterations in growth, production of anatomical and reproductive anomalies, changes in behaviour patterns, etc. The macroinvertebrates that are the most affected are the molluscs due to their high rate of bioaccumulation and to their low rate of purification. Within these, the most sensitive groups are the gastropods and the bivalves. In other taxonomic categories they follow to them in sensitivity, crustaceans, algae and fish. Nevertheless, no organism has so far shown the sensitivity that characterises neogastropods.

The magnitude of the effects of TBT and the repercussion of the legislation of their use were particularly remarkable in oysters and neogastropods. Specifically, the most devastating effects of TBT in the marine environment were observed on the curly or Japanese oyster, *Crassostrea gigas* and the coastal gastropod *Nucella lapillus* (snail multicoloured). The harmful effects of TBT on *Crassostrea gigas* were what set in motion the beginning of the legislation to control the use of this compound in the formulation of antifouling paints, a fact that is now a milestone in the recent history of environmental protection (Quintela, 2002).

The Bay of Arcachon (Atlantic coast of France) is one of the most important areas for the oyster breeding in the world and its economy depends on the sale both of oyster seeds and of the adults themselves. It produces from 10,000 to 15,000 metric tonnes of Japanese oyster, 10% of the French total production. During the summer season there is a great deal of maritime movement a dense marine occupation, with the number of pleasure ships sometimes reaching 15,000. At the end of the Sixties there began to be observed, occasionally, a thickening of the oyster shells and from 1974 on this was to be seen in all the oyster beds of the bay, affecting between 80 to 100% of the oysters. Between 1971-1986 a series of phenomena took place that severely damaged the oyster breeding in the area, such the appearance of physical anomalies (malformations in the shell characterised by the thickening of valves), reduction in individual oyster growth and drastic fall of the putting. Different studies consistently related these anomalies to contamination by TBT coming from antifouling paints.

The anomalies registered affected the calcification process and comprised the thickening of the shell because of the formation of chambers that contained gelatinous proteins in their interior so that the shell acquired a spherical and unpleasant aspect. The space destined for the body was reduced, which led to the oysters having less flesh on them. Both factors prevented the commercialisation of these bivalves, causing the collapse of oyster breeding from 1977 to 1981. In these circumstances, with a concentration of



TBT in water superior to 100 ng/l, the number of oyster breeders was reduced to half and the economic losses ascended to about 150 million dollars. The resulting profound socio-economic crisis caused French authorities to regulate the use of paints with a TBT base in January of 1982, which made it possible to gather a satisfactory number of oysters in summer, after five years of total loss of life of larvae.

The second paradigmatic case of the negative effects of TBT on organisms that, at the outset, were not the object of their action, is that of marine gastropods, and specifically the neogastropods. What has occurred here is the superimposition of masculine sexual characters on the females and which has received the name of *imposex*. In some species, this phenomenon negatively affects the reproductive ability so that, under certain conditions of contamination, the populations of the most sensitive species are doomed to disappearance.

One of the first impacts of exposure to TBT that was described was the masculinization of the females of neogastropods. This phenomenon was detected almost simultaneously in *Nucella lapillus* around 1970 in Plymouth Sound (England), *Nassarius obsoletus* in Long Island (the United States) and in *Erinacea Ocenebra* in Arcachon (France).

The term *imposex* was coined to denote that superimposition of masculine sexual characters on females. The first evidence of the bond between this phenomenon and the contamination by TBT did not appear until some ten years later. And it was not until the methods of analysis of organic derivatives of tin compounds were perfected that the sensitivity of TBT response became obvious. Multiple later studies have demonstrated that it is a widely extended event and at the present time it has been stated that some 150 species pertaining to approximately 78 genera, including the mesogastropods, show imposex.

When the females of *N. Lapillus* are exposed to TBT, they take place a masculinization proportional to the dose of polluting agent. A penis and a vas deferens begin to form. The vas deferens extends towards the oviduct and can even actually block it, making it impossible for the egg capsules to come out so that the females functionally become sterile. In extreme cases the bursa copulatrix can even be substituted by a prostate. Finally, the accumulation of the aborted egg capsules causes a trauma that leads to the death of the animal, which is why in highly affected populations there is a low proportion of females.

Both this lessening of the number of females in the populations and, mainly, the sterility of the females affected by advanced stages of imposex entail a decline in the populations of this gastropod. As it is a species of direct development, the lack of a planktonic phase negatively conditions the recovery of the populations, leading them to extinction in some cases.

Minimum amounts of TBT have been found in whales, dolphins and members of the seal family in the United States, Southeast Asia, the Adriatic Sea and the Black Sea,





absorbed through the nutritional chain. In addition, tributyltin reduces the resistance to infections in fish like plaice and other flat fish that live at the bottom of the sea and which are exposed to relatively high levels of TBT, especially in those areas with muddy sediments as is the case of ports and estuaries.

#### 4. CONSEQUENCES OF VOLATILE ORGANIC COMPOUND (VOC) USE IN ANTIFOULING COATINGS

The only required function of the constituent volatile vehicle of a liquid paint is to allow it to be elaborated and applied. Both the resins or oils, and the solvent free products, form in general solid or semisolid materials that could not be applied by any of the procedures normally used, such as brushes, rollers or pistol.

Generally, the composition of the volatile vehicle in paints responds to a mixture or combination of different solvents. Real resin or fixed vehicles solvents do exist, as do other organic products which, although not fixed vehicle solvent, are used together with the former as paint extenders. The purpose of including these extenders in the formulation of paints, is to improve the application properties and to be able to properly control the evaporation rate of the volatile vehicle during the drying. Their being volatile, the action of solvents is based on their power to dissolve non-volatile organic substances, without either of them experiencing any chemical modification, with the latter being extended in film form after the evaporation has taken place (González, 1994).

The organic chemical agents normally used, like solvents or extenders, belong fundamentally to one of the following types: (Velo, 1996)

- *Petroleum by-products*: aliphatic solvents. Benzine and gasoline are of this type, their being characterised by being insoluble in water, liquid, colourless and with a characteristic smell
- *Soft coal-tar by-products*: aromatic solvents. Benzol and solvent gasoline are of this type, their physical appearance being very similar to that of the petroleum by-products. Chemically, benzol is the aromatic hydrocarbon benzene  $C_6H_6$ , while solvent gasoline contains xylene and superior benzene homologs
- *Organic compounds*. Within this group, obtained by means of deferential chemical processes such as the fermentation, distillation, presence of catalysts, alkaline means, etc., are the *Alcohols*, the *Esters*, the *Ethers* and the *Ketones*.

The need to watch the concentrations of VOC fundamentally derives from their own toxicity, since the use of solvents gives rise to emissions of organic compounds in to the atmosphere that can be harmful to health and produce important damage to natural resources. Most volatile organic compounds (VOC) are harmful to ozone and some of them are known cancerigenic agents, which is why it is necessary to reduce their emissions in to the atmosphere. Therefore, the paints being a source of VOC because of solvent evaporation, it has become necessary to consider these compounds as polluting elements when it comes to formulating and manufacturing the paints, no matter what kind they are.

## 5. REGULATIONS ON THE MANUFACTURE AND USE OF ANTIFOULING COATINGS

The problems of pollution caused by the TBT present in antifouling paints was dealt with for the first time in the OMI Committee for the Protection of the Marine Environment (CPMM) in 1988, when the Paris 8 Commission asked the OMI to study the need to elaborate measures within the framework of the pertinent legal instruments in order to limit the use of TBT compounds in the seafaring ships. By then there was unequivocal proof on a world-wide scale that tributyltin and other organic by-products of tin compounds were detrimental for aquatic organisms and several countries had already adopted measures either individually or within the framework of regional agreements in order to try to reduce the detrimental effects of antifouling paints containing tributyltin. However, it was clear that it would be necessary to establish international measures to regulate the use of antifouling paints, and in April of 1990, in the Third international symposium on organic by-products of tin compounds, held in Monaco, it was recognised that the OMI was the appropriate organ to carry out that task.

In 1990, in its 30<sup>th</sup> Sessions, the CPMM adopted the resolution MEPC.46(30) on *“measures to resist the possible adverse effects of the use of tributyltin compounds in antifouling paints”*. In this resolution governments were recommended to adopt measures to eliminate the use of antifouling paints containing compounds of tributyltin in ships of under 25 m in length and whose hull is not of aluminium, and to eliminate the use of antifouling paints whose average rate of leaching is higher than 4 micrograms of tributyltin per cm<sup>2</sup>/day.

In 1990, the CPMM of the OMI received the results of a control study of tributyltin, which confirmed the toxicity of tributyltin compounds in marine organisms. The Committee also received information on other existing antifouling systems, which included data on their effectiveness and the risk that they are for the aquatic environment.

In the 38<sup>th</sup> session, held in 1996, the CPMM established a work group by correspondence so that it could study the pertinent issues. The main conclusions based up on the observations of the 12 countries and four nongovernmental organisations taking part, were presented to the Committee in its 41<sup>st</sup> session, held in April of 1998.

In the 42<sup>nd</sup> session, held in November of 1998, the CPMM approved a draft resolution of the Assembly that includes the year 2008 as a deadline for the total prohibition of compounds of organic tin by-products used as biocide in the antifouling systems for ships.

The draft resolution, elaborated by the Work Group that met during the 42<sup>nd</sup> session of the CPMM, was presented at the 21<sup>st</sup> Assembly of the OMI, which was held in November of 1999. In this draft resolution the OMI *“urges the Committee for the Protection of the Marine Environment to adopt whatever measures may be necessary to elaborate as quickly as possible a legally binding world-wide scale instrument with the purpose of solving the question of the detrimental effects of the antifouling systems used on ships”*.



In addition, the OMI “*decided that the instrument of world-wide character that the Committee for the Marine Environment elaborates would have to guarantee, on a world-wide scale, the prohibition of the application on ships of organic by-products of tin compounds used as biocide in the antifouling systems on ships, by January 1<sup>st</sup> 2003 at the latest, and the complete prohibition of the presence on ships of organic by-products of tin compounds used as biocide in the antifouling systems, by January 1<sup>st</sup> 2008 at the latest*”.

As regards VOC, we can make reference to the Royal Decree 117/2003, of January 31<sup>st</sup>, on the limitation of volatile organic compound emissions due to the use of solvents in certain activities.

The use of solvents in certain activities causes emissions of organic compounds to be released into the atmosphere and which can be injurious to health and produce considerable damage to the natural resources. Bearing in mind the above, the Council of Ministers of the European Union approved, on March 11<sup>th</sup> 1999, the Directive 1999/13/CE, the aim of which is to prevent or to reduce the harmful effects for people and the environment stemming from those activities that use large quantities of organic solvents in their manufacturing processes or work.

This Directive lays down certain specific regulations for those plants wishing to carry out the above activities, and among which there appear: (i) that of not exceeding the different maximum emission raking for volatile aromatic hydrocarbon emission (hydrocarbons that, under normal conditions of pressure, have a boiling point equal or inferior to 250 °C and which at least have an aromatic ring in its devised structural formula), which will be equal or inferior to 0.5 % of the product; (ii) the one to reduce their emissions by other means, such as using products with a low solvent content or solvent-free. Likewise, the maximum volatile organic compound content (VOC) will be equal or lower to 200 g/l minus the water. The unit used for the VOC content is “mass in grams of COV per litre of product (g/l minus the water).

## **6. FUTURE PROPOSALS**

### **6.1. FROM SOLVENTS TO WATER**

Theoretically it is possible to replace all the solvent-based products that are traditionally on the market with water-based ones.

Solvent-based paints have: (i) high tolerance in their application and drying under adverse conditions, like, for example, low temperature, discharge humidity; (ii) good behaviour on difficult substrates, such as very deteriorated surfaces; (iii) good application properties; (iv) good mechanical or chemical resistance; (v) good aesthetic appearance. Nevertheless, the technology for water-based is constantly improving.

It is also possible to produce solvent-based products with a lower solvent content by using the modern technology for high solid contents that can be used to formulate products that offer many of the properties attributed to the traditional solvent-based products,



but which significantly reduce the solvent content. Although they are more expensive and normally they dry more slowly, they can play an important role in the reduction of emissions. The use of VOC in water-based paint is normally vital for the behaviour of the product and this is particularly true of water-based products that have been formulated to replace the solvent-based ones. Given the present low levels of VOC in water-based products, any reduction that might occur would not be significant to the total amount of the reduction of VOC emissions.

Water-based products are being researched and, together with the high solid content products, are replacing the traditional solvent-based products. It is still possible to achieve even greater reductions in VOC emission by reducing the volatile organic compounds in water-based and solvent-based products and by increasing the use of water-based or high solid content paints. Nevertheless, this will take time. The industry will need to reformulate an important and wide part of its existing product range, and this can only be achieved over a period of several years. What is more, a greater reduction will mean greater changes in products, in application techniques and in the characteristics of its uses. The changes will also have economic consequences originating from the increase in R+D costs and raw materials and will require new investment in equipment.

## 6.2. ALTERNATIVES TO ORGANIC BY-PRODUCTS OF TIN COMPOUNDS

The antifouling systems that do not contain TBT can be made up of soluble marine water matrices that contain biologically active tin free ingredients. The biocides disperse and remain contained within the matrix, although they are not necessarily bound to it via a chemical link. In the sea-water/paint interface, the biocide leaches at a controlled rate. The matrix dissolves and releases new biocide, which allows a predictable yield to be obtained.

The main options available at the present time are the following ones:

- *Antifouling copper-based paints.* The copper is a thousand times less detrimental than TBT, which is why, even if other options were not considered, the change over to copper-based products would immediately benefit the marine environment. Their drawback is that they are only effective against the marine fauna, it being necessary to fight the growth of algae with pesticide, which can create new threats to the environment.
- *Tin-free antifouling paints.* They are indicated for those ships that enter dry-dock every three and a half years or more frequently since they tolerate a certain amount of biological incrustations. They give a good result on specialised ships such as tugboats, pilot boats, dinghies and research ships of investigation, if these are used at least 100 days a year and enter dry-dock at least every three years. When their use is not so frequent, there is a greater risk of biological incrustation and the ship would have to enter dry-dock every year.



- *Antiadherent coatings.* They do not contain biocides but their surface is very slippery, which prevents biological incrustations and makes washing them down easy when it has to be done. They are preferably for ships with a minimum speed of 30 knots. Once damaged, the coating is difficult to repair. Small incrustations form, which are easy to clean with compressed air hoses in the annual overhaul in dry-dock.

- *Cleaning.* The periodic cleaning of the hull is a very appropriate solution for those ships that sail both on the sea and in fresh water, and in zones where few organisms adhere to the hull. For the cleaning of the merchant ships there are divers who use revolving brushes or compressed air hoses.

- *Electricity.* On creating a difference in the electrical charge between the hull and the seawater a chemical process that prevents biological incrustations is activated. This technology has proved itself to be more effective than tin free paint to prevent biological incrustations, but the system is expensive and is easily damaged. It also creates a greater risk of corrosion and requires a greater consumption of energy.

- *Coatings with prongs.* It includes coatings with microscopic prongs. Its effectiveness depends on the length and distribution of the prongs, although it has been demonstrated that these do stop certain crustaceans and algae adhering to the hull without causing any damage at all to the environment. However, the prongs could increase the resistance of the ship to the water. The use of surfaces with prongs on static objects such as on buoys and cooling water inlets could well be a realistic option for the future.

- *Natural resistance, natural biocides.* This is the substance produced by nature and which prevents biological incrustations or makes the incrustation process difficult. It is based on the ability of certain marine organisms, such as corals and sponges, to remain free of incrustations. Research relative to the use of natural compounds is still in an initial phase, although some active metabolites have already been identified and new biocides synthesised. The enzymes can stop bacteria from adhering to the hull (the first stage of incrustation growth), whereas the hydrophilic coatings have been based on the preference shown by biological incrustations for hydrophobic surfaces, such as rocks and the ships.

At the present time, we are testing different natural compounds extracted from the marine environment itself to see how effective they can be as biocides in antifouling paints, in a research project by the Ministry of Science and Technology of Spain through Project REN-0519/TECNO entitled “*Application of marine biotechnology in the production of environmentally innocuous antifouling coatings*”, in which the Department of Sciences and Techniques of Navigation and Shipbuilding of the University of Cantabria is taking part, Harbour Authority of Santander, the Cantabrian paint company Ferroluz S.A., the Scottish laboratory Ecossearch (International) Ltd. and the Department of Biological Sciences of the University of Heriot-Watt are also collaborators in the project.

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## SISTEMAS ANTIINCRUSTANTES: HACIA LA PRODUCCIÓN DE RECUBRIMIENTOS MEDIOAMBIENTALMENTE INOCUOS

### RESUMEN

Conocido el fenómeno del biofouling, así como las negativas consecuencias que supone para las estructuras artificiales en contacto con agua de mar en forma de defectos estructurales y de gastos adicionales para las empresas que desarrollan su labor en el ámbito marítimo debidos a los procesos de limpieza y prevención, la evolución en el mundo de la tecnología de las pinturas antiincrustantes, analizados los problemas medioambientales graves provocados por el uso indiscriminado de biocidas de alta toxicidad en su composición como son los compuestos organoestánicos y por la emisión incontrolada de compuestos orgánicos volátiles (COVs) a la atmósfera, atendiendo a la normativa medioambiental actual, tiene como única alternativa el desarrollar recubrimientos medioambientalmente inocuos en base agua en los que se utilicen como compuestos biocidas extractos del propio medio marino.

**Palabras Clave:** Biofouling, pinturas antiincrustantes, compuestos organoestánicos, compuestos orgánicos volátiles (COVs), normativa medioambiental

### INTRODUCCIÓN

Toda estructura artificial en contacto con agua de mar es rápidamente cubierta por una biopelícula microbiológica que sirve como base de asentamiento de macroorganismos. Este fenómeno, conocido como biofouling, causa problemas estructurales graves y su mitigación acarrea un severo gravamen económico para las industrias que operan en el medio marino.



Son cientos las especies que pueden formar parte del biofouling, fijándose al sustrato desarrollando un rápido crecimiento y gran potencial reproductor. Como consecuencia, el biofouling acelera los procesos de corrosión de los materiales y provoca pérdidas en la eficacia operativa de las estructuras en contacto con agua de mar. En las embarcaciones se incrementa la fricción entre el casco y el agua lo que comporta un aumento del consumo de combustible y la pérdida de velocidad y capacidad de maniobra.

Para evitar las pérdidas económicas, así como un deterioro acelerado de las estructuras artificiales en contacto con agua de mar, vienen empleándose distintos tipos de protecciones desde antiguo. Entre ellas destacan los revestimientos de cobre que comenzaron a ser utilizados por los fenicios y que siguieron empleándose con éxito hasta el siglo XVIII sobre embarcaciones de madera. Con la aparición de los buques de hierro comenzaron a elaborarse pinturas en las que el sulfato de cobre actuaba como principio biocida. A partir de 1960 se extendió el uso de pinturas en cuya composición podíamos encontrar cobre, mercurio, arsénico, derivados organoestánicos (compuestos orgánicos del estaño como el tributilestaño (TBT) y la trifeniltina (TPT)), las cuales con el paso del tiempo, se ha podido comprobar que suponían un riesgo real para el ecosistema marino.

En la década de los setenta se extendió el empleo de recubrimientos antiincrustantes basados en la actuación biocida de los derivados organoestánicos, en especial del tributilestaño (TBT), por lo que la mayoría de los buques de navegación marítima recubrieron sus cascos con este tipo de pinturas, que resultaron ser eficaces y económicas.

Durante la década de los ochenta se tomó conciencia de las consecuencias que el uso del TBT en las pinturas antiincrustantes estaba teniendo sobre los ecosistemas marinos, especialmente en áreas de bajo intercambio de agua por influencia mareal, como bahías o estuarios, donde resulta especialmente perjudicial sobre las poblaciones de algunos invertebrados, moluscos, crustáceos y peces, detectándose malformaciones muy importantes en algunas especies. Como consecuencia de la preocupación desatada ante estos hechos, varios países introdujeron controles para limitar el uso de TBT en las pinturas antiincrustantes en los buques pequeños. Así, en 1982, Francia prohibió el uso de TBT en los buques con una eslora inferior a 25 m, siguiendo su ejemplo Japón, Reino Unido, Estados Unidos, Noruega, Australia, Nueva Zelanda y otros países.

A principios de los años noventa, una resolución de la OMI recomienda a los gobiernos la prohibición del uso de tributilestaño en los buques de eslora inferior a 25 m y se imponen restricciones en el proceso de lixiviación del tributilestaño, debiendo de ser inferior a 4 microgramos por  $\text{cm}^2$  /día. Países como Japón, Nueva Zelandia y Australia prohíben el uso de antiincrustantes que contengan TBT (OMI, 1999).

En 1997, Japón prohíbe la fabricación de pinturas antiincrustantes que contengan TBT, siendo el 1 de enero de 2003 la fecha propuesta para la prohibición del uso de compuestos organoestánicos como biocidas en los sistemas antiincrustantes, quedando para el año 2008 su total prohibición.



## TECNOLOGÍA DE LAS PINTURAS ANTIINCRUSTANTES

Las pinturas antiincrustantes están especialmente formuladas para aplicar sobre estructuras en contacto con agua de mar e impedir el asentamiento de los organismos marinos que componen el biofouling.

Popularmente se las conoce con el nombre “*patentes*” y como todas las pinturas están formadas por un vehículo fijo, un vehículo volátil, pigmentos y aditivos. Una vez aplicadas forman una película seca, uniforme y bien adherida al sustrato a proteger y al entrar en contacto con el agua de mar, comienzan a liberar productos biológicamente activos que envuelven la superficie tratada en un manto biocida que impide la fijación de los organismos. La capacidad de control del nivel de liberación de las sustancias biocidas nos permitirá diferenciar varios tipos de pinturas antiincrustantes, siendo la concentración de toxinas en la capa de agua laminar (superficie de pintura en contacto con el agua de mar) la que determina el poder antiincrustante de la pintura. Factores como la velocidad del buque, la temperatura, salinidad y pH del agua de mar, iluminación, niveles de contaminación, etc., van a influir de manera notable en que dicha concentración de toxinas sea mayor o menor.

Las pinturas antiincrustantes las podemos clasificar como *no pulimentantes de matriz soluble o insoluble y autopulimentantes*.

### CONSECUENCIAS DEL USO DE COMPUESTOS ORGANOESTÁNNICOS COMO BIOCIDAS EN LAS PINTURAS ANTIINCRUSTANTES

En general todos los compuestos orgánicos del estaño, y en particular el tributilestaño (TBT), son compuestos extremadamente tóxicos, incluso a concentraciones de pocos nanogramos por litro. La magnitud de los efectos del TBT y la repercusión sobre la legislación de su uso fueron particularmente destacables en las ostras y los neogasterópodos, aunque también se han encontrado cantidades mínimas de TBT en ballenas, delfines y miembros de la familia de las focas en los Estados Unidos, sudeste asiático, Mar Adriático y Mar Negro, absorbido a través de la cadena alimenticia. Además, el tributilestaño reduce la resistencia a las infecciones en peces como la platija y otros peces planos que habitan en el fondo del mar y que están expuestos a niveles relativamente altos de TBT, en particular en las zonas con sedimentos limosos como es el caso de puertos y estuarios.

### CONSECUENCIAS DEL USO DE COMPUESTOS ORGÁNICOS VOLÁTILES (COVS) EN LAS PINTURAS ANTIINCRUSTANTES

El vehículo volátil constituyente de una pintura líquida, tiene como única misión permitir su elaboración y aplicación. Tanto las resinas o aceites, como los productos exentos de disolvente, forman en general materiales sólidos o semisólidos que no podrían ser aplicados por cualquiera de los procedimientos normalmente utilizados, tales como brocha, rodillo o pistola.





La necesidad de vigilar las concentraciones de COVs se deriva fundamentalmente de su propia toxicidad, ya que el uso de disolventes da lugar a emisiones de compuestos orgánicos a la atmósfera que pueden ser nocivas para la salud y producir importantes perjuicios a los recursos naturales. La mayoría de los compuestos orgánicos volátiles (COVs) son precursores del ozono y algunos de ellos son conocidos agentes cancerígenos, por lo que es necesario disminuir sus emisiones a la atmósfera. Por lo tanto, siendo las pinturas una fuente de COVs por evaporación de disolventes, se hace necesario considerar como elemento contaminante estos compuestos a la hora de formular y fabricar las pinturas, sean de la naturaleza que sean.

### **NORMATIVA RELATIVA A LA FABRICACIÓN Y USO DE PINTURAS ANTIINCRUSTANTES**

Los problemas de contaminación causados por el TBT presente en las pinturas antiincrustantes se trató por primera vez en el Comité de Protección del Medio Marino (CPMM) de la OMI en 1988, cuando la Comisión de París 8 solicitó a la OMI que estudiase la necesidad de elaborar medidas en el marco de los instrumentos jurídicos pertinentes para limitar el uso de los compuestos de TBT en los buques de navegación marítima.

En 1990, en su 30º periodo de sesiones, el CPMM adoptó la resolución MEPC.46(30) sobre *“medidas para contrarrestar los posibles efectos adversos del empleo de compuestos de tributilestaño en las pinturas antiincrustantes”*. En dicha resolución se recomienda a los gobiernos que adopten medidas para eliminar el empleo de pinturas antiincrustantes que contengan compuestos de tributilestaño en los buques de eslora inferior a 25 m y cuyo casco no sea de aluminio, y eliminar el empleo de pinturas antiincrustantes cuya tasa media de lixiviación sea superior a 4 microgramos de tributilestaño por  $\text{cm}^2/\text{día}$ .

El proyecto de resolución, elaborado por el Grupo de trabajo que se reunió durante el 42º periodo de sesiones del CPMM, se presentará a la vigésima primera Asamblea de la OMI, que se celebrará en noviembre de 1999. En dicho proyecto de resolución la OMI “insta al Comité de Protección del Medio Marino a que adopte las medidas necesarias para elaborar de forma rápida un instrumento jurídicamente vinculante a escala mundial con el fin de resolver la cuestión de los efectos perjudiciales de los sistemas antiincrustantes utilizados en los buques”. Además la OMI “decide que el instrumento de carácter mundial que elabore el Comité de Protección del Medio Marino debería garantizar la prohibición a escala mundial de la aplicación en los buques de compuestos organoestánicos utilizados como biocidas en los sistemas antiincrustantes en los buques, el 1 de enero de 2003 a más tardar, y la prohibición completa de la presencia en los buques de compuestos organoestánicos utilizados como biocidas en los sistemas antiincrustantes, el 1 de enero de 2008 a más tardar”.

En cuanto a los COVs podemos hacer referencia al Real Decreto 117/2003, de 31 de enero, sobre limitación de emisiones de compuestos orgánicos volátiles debidas al uso de disolventes en determinadas actividades.



## PROPUESTAS DE FUTURO DEL DISOLVENTE AL AGUA

Teóricamente es posible sustituir todos los productos que tradicionalmente están en el mercado de base disolvente por versiones en base agua.

También es posible producir productos de base disolvente con un menor contenido de disolvente utilizando la moderna tecnología de altos contenidos en sólidos que puede ser usada para formular productos que ofrecen muchas de las propiedades que se atribuyen a los tradicionales productos en base disolvente, pero que reducen significativamente el contenido de disolvente.

### ALTERNATIVAS A LOS COMPUESTOS ORGANOESTÁNNICOS

Los sistemas antiincrustantes que no contienen TBT pueden estar compuestos por matrices solubles de agua marina que contienen ingredientes libres de estaño biológicamente activos. Los biocidas se dispersan y quedan contenidos en la matriz, aunque no estén necesariamente ligados a ella mediante un enlace químico. En la interfaz agua marina/pintura, el biocida se lixivia a un ritmo controlado. La matriz se disuelve y libera nuevo biocida, lo que permite lograr un rendimiento predecible.

Las principales opciones de que se dispone en la actualidad son las siguientes:

- *Pinturas antiincrustantes a base de cobre.*
- *Pinturas antiincrustantes libres de estaño.*
- *Revestimientos antiadherentes.*
- *Limpieza..*
- *Electricidad.*
- *Revestimientos con púas.*
- *Resistencia natural, biocidas naturales.*

En la actualidad, estamos ensayando la eficacia como biocidas en pinturas antiincrustantes de diferentes compuestos naturales extraídos del propio medio marino, en una investigación financiada por el Ministerio de Ciencia y Tecnología de España a través del Proyecto REN-0519/TECNO titulado «*Aplicación de biotecnología marina en la producción de recubrimientos antiincrustantes medioambientalmente inocuos*», en el que participa el Departamento de Ciencias y Técnicas de la Navegación y de la Construcción Naval de la Universidad de Cantabria y colaboran la Autoridad Portuaria de Santander, la empresa cántabra de pinturas Ferroluz S.A., el laboratorio escocés Ecossearch (International) Ltd. y el Departamento de Ciencias Biológicas de la Universidad de Heriot-Watt.